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Accumulation of acid sites on natural clinoptilolite under recurring dehydration

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Abstract A new ^1H NMR approach was applied to study the influence of recurring dehydration on the acidity of a natural Ca-rich zeolite clinoptilolite. It has been found that thermal cycling progressively increases the rate of the proton exchange between water molecules in the rehydrated state. The observed effect is interpreted as a result of the irreversible accumulation of specific structural defects represented by Brønsted acid sites: each dehydration at 720 K adds to the acid sites in an amount of the order of 10^{-3} per unit cell. The number of these defects, detected by NMR in hydrated mineral, is in reasonable agreement with their amount estimated for the dehydrated state with an IR-spectroscopy CO-probe method. A comparison of the results obtained for two distinct zeolite samples shows that the Ca^{2+} ions are of first importance in the dehydration-induced formation of the active acid sites. The barrier for the proton-transfer reaction between the acid sites and H_2O molecules in hydrated clinoptilolite is found to be 46 kJ mol^{-1} , which is not too different from the value of 54 kJ mol^{-1} reported recently for natural chabazite.

Keywords Zeolite · Clinoptilolite · Cyclic dehydration–rehydration · Acid sites · NMR · IR spectroscopy

Introduction

The response of a natural zeolite to thermal dehydration is determined by many factors including the framework topology, Al,Si distribution, nature and content of extra-framework cations, etc. This problem has been largely investigated by Van Reeuwijk (1972) and reviewed in detail in a more recent paper by Bish (1995). An essential aspect of dehydration is the concomitant formation of various defects, partly irreversible, which may modify physicochemical properties of zeolite. This may be exemplified by the random breakage of some tetrahedral cation–oxygen bonds. Other defects of this kind are the active acid sites (H centers) which determine the catalytic properties of zeolites. Up to now, basic studies of the acid sites have been carried out on dehydrated zeolites, the question of the behavior of H centers at subsequent rehydration still remaining obscure, especially in natural zeolites.

IR spectra of the absorbed probe molecules, for example CO, are commonly used to trace the Lewis and Brønsted acid sites in anhydrous zeolites (see, e.g. Colluccia et al. 1999). Recently, we developed an NMR approach to obtain precise measurements of the rate of the proton-transfer reaction between the water molecule and H-center in hydrated zeolites. This allows one to detect the acid sites even at extremely low concentrations (Afanassyev et al. 2000). In the present study we applied both these methods to studying the formation of the active acid sites in natural clinoptilolite during the process of cyclic dehydration–rehydration, which is essential for many practical applications. We have chosen clinoptilolite as one of the most abundant and commercially important zeolites. Structural details of the dehydration process in clinoptilolite have been investigated in some other works (Koyama and Takéuchi 1977; Armbruster and Gunter 1991; Armbruster 1993).

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Experimental

The clinoptilolite specimen was from agate (Tedzami, Republic of Georgia), with chemical composition $\text{Na}_{2.6}\text{K}_{0.5}\text{Ca}_{1.7}[\text{Al}_{6.5}\text{Si}_{29.5}\text{O}_{72}]\cdot 20.8\text{H}_2\text{O}$. According to X-ray single-crystal analysis, its unit cell has dimensions $a = 17.621(3)$ Å, $b = 17.927(2)$ Å, $c = 7.3984(7)$ Å, $\beta = 116.41(1)^\circ$, $V = 2093.2$ Å³, in rough agreement with the data reported by Armbruster and Gunter (1991) for a heulandite–clinoptilolite sample with similar composition. The sample was subjected to repeated dehydration–rehydration on air in a platinum crucible: in each cycle it was heated to 720 K at a rate of 8 K min^{-1} and held at this temperature for 2 h, then the sample was cooled to room temperature and rehydrated overnight at $P(\text{H}_2\text{O}) \approx 7$ mm Hg, which proved enough to gain constant weight. A sequence of five cycles was applied. As follows from our weight-loss measurements, at 720 K the H_2O remainder in clinoptilolite was about 1.5 molecules per unit cell in each cycle.

Portions of the sample in the initial state and after each rehydration were analyzed by NMR spectroscopy. Broad-line ^1H NMR spectra, resulting mainly from the intra-molecular magnetic dipole–dipole interactions of the H_2O protons, were recorded in the form of the first derivative of the NMR absorption line by sweeping the frequency in the neighborhood of 25 MHz using a home-made NMR spectrometer with signal accumulation. The experiments were carried out in the temperature range from 295 to 410 K, corresponding to intense H_2O self-diffusion. A fast diffusive motion of water molecules in noncubic crystal offered possibilities for applying our approach to examine the proton-transfer reactions in the clinoptilolite cavities.

IR absorption spectra were recorded for the original and treated (five heating–cooling cycles) samples using a Shimadzu FTIR-8300 spectrometer. A self-supported pellet ($18\text{--}30\text{ mg cm}^{-2}$) was placed into a quartz cell connected to a vacuum unit and pumped at $10^{-4}\text{--}10^{-5}$ mm Hg for 1 h. Then the cell was heated at a rate of 8 K min^{-1} to 700 K, kept for 1 h at pumping, cooled to 77 K, and IR spectra were accumulated at different CO pressures. As might be expected from many previous zeolite studies (Razdobarova and Paukshtis 1991; Sobolev et al. 1996; Carron et al. 1998), the heating under pumping before IR-spectra registration does not cause any significant formation of additional active sites.

A series of the above experiments was also performed on a zeolitic tuff from Hector, USA, of a bulk composition $\text{Na}_{5.3}\text{K}_{0.7}\text{Ca}_{0.2}\text{Mg}_{0.2}\text{Fe}_{0.3}\text{Al}_{6.1}\text{Si}_{29.5}\text{O}_{72}\cdot 19.6\text{H}_2\text{O}$, constituted mainly by Capoor clinoptilolite; this sample contained also an admixture of mordenite and other small impurities.

Results and discussion

Ca-rich clinoptilolite

The powder ^1H NMR spectra of the Tedzami clinoptilolite (Fig. 1) display a fine structure typical of zeolites, in which H_2O molecules execute fast jumps through different structural positions. In this case, the spectrum is determined by the intramolecular dipole–dipole interaction of nuclear spins, partly averaged by molecular motion, and thus is a function of the spatial distribution of water molecules in the zeolite channels (Ducros 1960; Gabuda and Lundin 1968). From line-shape analysis (Moroz et al. 2001), the principal values of the dipolar coupling tensor at room temperature are: $S_{zz} = 14.9 \pm 0.2$ kHz, $S_{yy} = -8.5 \pm 0.1$ kHz, $S_{xx} = -6.4 \pm 0.1$ kHz for the initial sample and remain practically unchanged for the samples subjected to cyclic dehydration–rehydration. This means that the

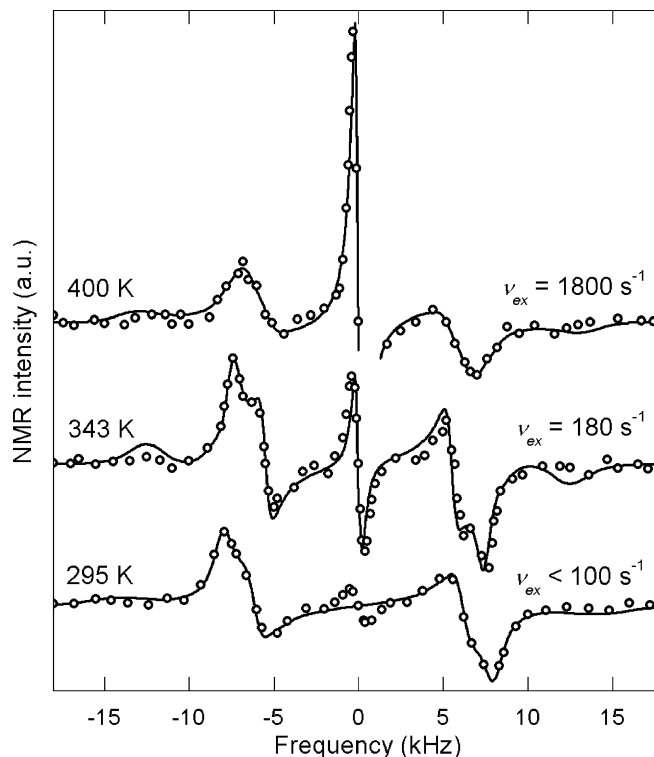


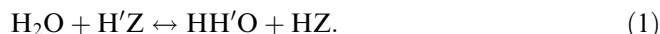
Fig. 1 Experimental NMR absorption derivatives (circles) at different temperatures for the sample of Tedzami clinoptilolite, subjected to five dehydration–rehydration cycles. The calculated spectra for different rates of proton exchange are shown as solid lines

thermal treatment does not lead to a notable change of water arrangement.

An enhancement of H_2O diffusive mobility with temperature makes the doublet structure of the spectrum more pronounced (Fig. 1) with a small decrease in the S_{ij} values. However, further heating leads to a smearing-out of the fine structure, accompanied by building up the peak in the spectrum center. This spectrum evolution is typical of the development of proton exchange in the water subsystem, which suppresses the effect of the intramolecular dipolar proton–proton interaction. From 290 to 410 K, the exchange-induced transformation of the NMR spectrum is not significant (if present) in the initial sample, but becomes progressively more obvious after each cycle of dehydration–rehydration. By applying the analysis described in detail in a recent publication (Afanassyev et al. 2000), the frequency ν_{ex} , with which one of the H_2O protons is substituted by some exterior proton, was determined. As shown in Fig. 2a, the temperature dependencies of ν_{ex} , obtained after different cycles, correspond to an Arrhenius equation with the same activation energy $U_a = 46 \pm 5\text{ kJ mol}^{-1}$ but with a variable preexponential factor, ν_{ex}^0 . It can be seen from Fig. 2b that the ν_{ex}^0 value is approximately proportional to the cycle number. [We failed to obtain the $\nu_{ex}(T)$ dependence for the initial sample, where an assessment $\nu_{ex} \leq 2 \times 10^2\text{ s}^{-1}$ was made only for 400 K].

As in the above-mentioned instance of chabazite, we suppose that (1) the observed proton exchange is due to

the H₂O interaction with Brønsted acid sites Al–O(H)–Si. (2) The equilibrium state of the defect of interest corresponds to a neutral adsorption structure in which the water molecule is H-bonded with the zeolitic proton (HZ), and the interaction discussed consists of the proton transfer from one zeolite oxygen atom to the water molecule and the subsequent or simultaneous return of one of the molecular protons to another oxygen site (Krossner and Sauer 1996; Sauer 1996):



In the course of this process, the hydrated H₃O⁺ ions (ion-pair complexes) may arise as a transition state of the reaction. (3) Under high-hydration conditions ($T \leq 400$ K), the concentration of HZ remains unchanged at temperature variations.

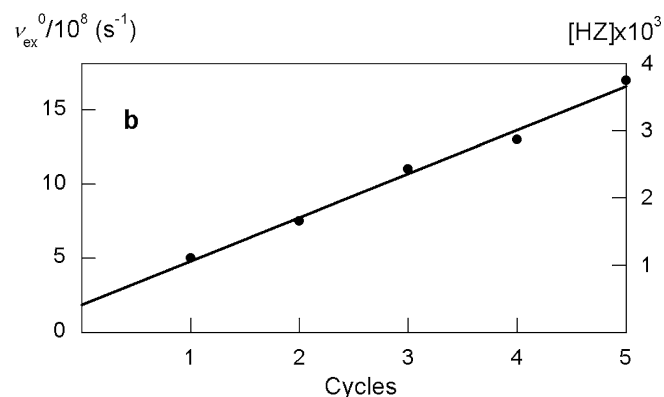
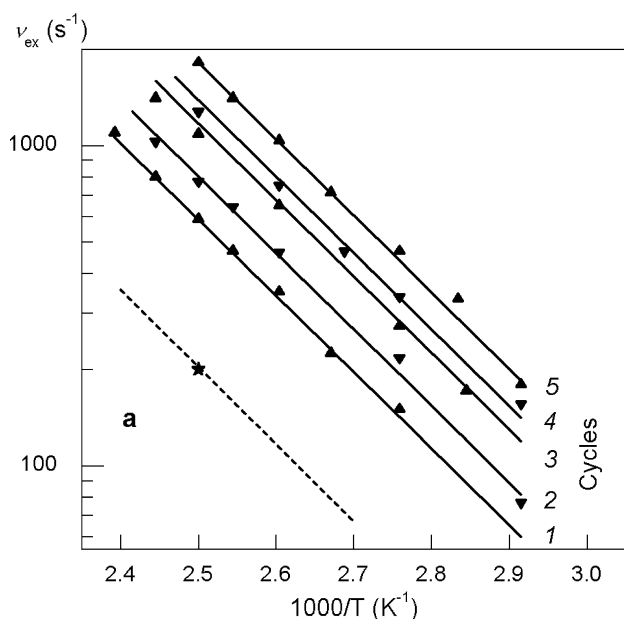


Fig. 2a, b a Arrhenius plots of the proton-exchange frequency, obtained after each rehydration of Tedzami clinoptilolite. *Solid lines* are linear fits of the data with the same activation energy $U_a = 46$ kJ mol⁻¹; the dependence estimated for the initial state is shown as *dashed line*. **b** Preexponential factor v_{ex}^0 as a function of the dehydration–rehydration cycle. The *right-hand scale* shows the corresponding change in the amount of acid sites, derived with Eq. (2)

In the context of these assumptions, the increase of v_{ex}^0 with the cycles of thermal treatment has to be associated with the formation of a portion of active acid sites during each dehydration process. The concentration of these sites in the rehydrated states can be extracted from the relation:

$$v_{ex}^0 \approx \bar{v}_{ex}^0 [\text{HZ}] / [\text{H}_2\text{O}], \quad (2)$$

where \bar{v}_{ex}^0 is a mean preexponential factor characterizing the proton transfer within the local adsorption structure, taken for 10^{13} s⁻¹ (Afanassyev et al. 2000). Based on this assessment, the amount of Brønsted centers in each cycle was estimated upto a scaling factor of 2 or 3 (the right-hand scale on Fig. 2b). The extrapolation of the obtained linear dependence to the untreated initial state gives $[\text{HZ}] \approx 4 \times 10^{-4}$ per unit cell (that is by an order less than previously found in natural chabazite). From this value the expected rate of proton exchange at 400 K in the original sample is about 2×10^2 s⁻¹, that is, close enough to the experimental limit of v_{ex} given above for this temperature. This enables one to extend the [HZ] additivity to all cycle sequences, in other words, to suppose that each dehydration gives rise to an excess of zeolitic protons in an amount of about 6×10^{-4} per unit cell.

For the thermally treated samples, IR spectra of the adsorbed CO molecules, obtained by subtracting the spectrum of dehydrated clinoptilolite without CO, display two distinct bands in the region of the OH-stretching vibrations (lines 4 and 5 on Fig. 3), which can be assigned, respectively, to two types of the adsorption OH...CO complexes (Carron et al. 1998). The narrow band at 3599 ± 5 cm⁻¹ most likely belongs to the loosely held complexes of terminal groups HO–Si with CO, whereas the broad band at 3245 ± 10 cm⁻¹ may be ascribed to the CO molecules forming a relatively strong bond with the active acid centers. In the region of C≡O vibrations, these complexes give rise to two closely spaced, overlapped bands at 2158 ± 1 cm⁻¹ (line 1) and 2171 ± 5 cm⁻¹ (line 2). The first line belongs to the complexes with terminal OH groups whereas the high-frequency line arises as a result of the strong interaction of CO molecules with the acid sites. A weak band at about 2230 cm⁻¹ (line 3) apparently arises from CO adsorbed on Al atoms, removed from the zeolite framework. From the intensity of line 4, the concentration of [HZ] in the dehydrated zeolite after five heating–cooling cycles can be derived as $(7 \pm 3) \times 10^{-3}$ per unit cell, in reasonable agreement with the above-described results of the NMR measurements (see Fig. 2b).

Ca-poor clinoptilolite

The ¹H NMR spectra of the Hector clinoptilolite have a rather complex shape representing a superposition of at least three distinct lines (Fig. 4). The first of them, related immediately to the clinoptilolite component, is close enough to that of the Tedzami sample. The second,

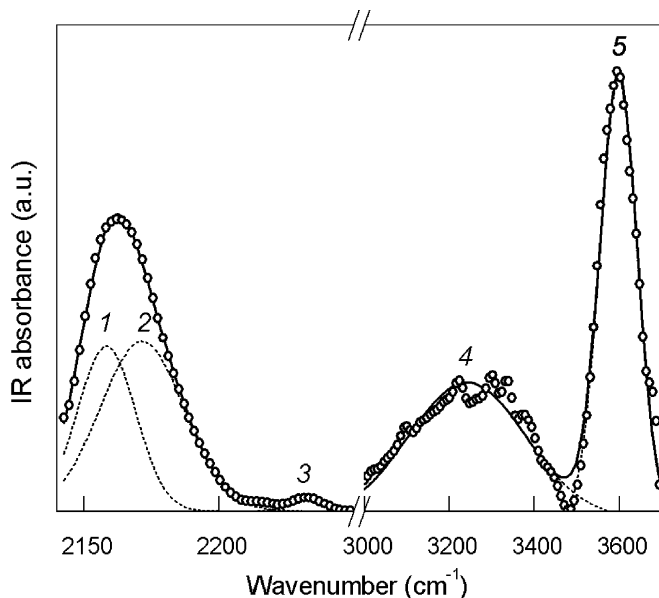


Fig. 3 Experimental (circles) and fitted (solid lines) fragments of the IR difference spectrum of CO adsorbed at pressure of 10 mm Hg on the thermally treated (five heating-cooling cycles) sample of Tedzami clinoptilolite. Dashed lines (1–5) show the decomposition of the observed spectrum into components assigned to different CO-adsorption complexes (see text)

which manifests itself in the frequency range ≤ 7 kHz and corresponds to a dipolar coupling tensor with the principal values $S_{zz} = 5.0 \pm 0.1$ kHz, $S_{yy} = -4.3 \pm 0.1$ kHz, $S_{xx} = -0.7 \pm 0.1$ kHz, can confidently be assigned to zeolite mordenite, $(\text{Na}_2, \text{Ca}, \text{K}_2)_4[\text{Al}_8\text{Si}_{40}\text{O}_{96}] \cdot 28\text{H}_2\text{O}$, based on special experiments carried out with the monomineral samples of this mineral. The decomposition of NMR spectrum into components implies that the mordenite admixture makes up about 15%. Finally, a peak at the spectrum center represents additional hydrogen-bearing impurities, for example, montmorillonite, present in minor amounts. At elevated temperatures, the mordenite spectral component transforms into a narrow single line, apparently due to the development of proton-transfer reactions. At the same time, no significant manifestation of the proton exchange was found up to 420 K in the clinoptilolite spectrum. Moreover, the clinoptilolite components of all NMR spectra for both initial and treated samples at each temperature are close to each other and can be calculated with good accuracy in the framework of an H_2O diffusion model (Moroz et al. 2001), implying that there is no formation of active OH groups in this sample on cyclic thermal treatment. The acid sites also escaped detection by IR spectroscopy: CO, adsorbed on the Hector samples, did not display any bands in the vicinity of 3250 and 2170 cm^{-1} .

It seems to be reasonable to associate the sharp contrast in the response of two clinoptilolite samples to cyclic dehydration-rehydration with a difference in their compositions, namely, in calcium content. As is clear from a large body of studies on synthetic zeolites (see,

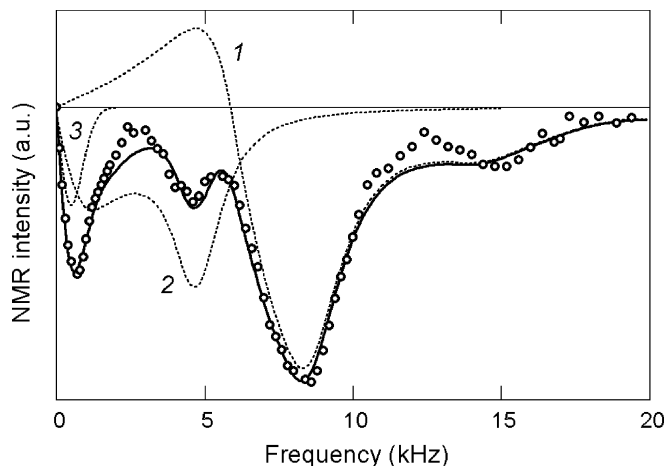


Fig. 4 Half-experimental ^1H NMR spectrum (circles) for the clinoptilolite tuff from Hector at room temperature. The fitted spectrum and its decomposition into components (1 clinoptilolite; 2 mordenite; 3 unidentified hydrogen-bearing impurity) are shown as solid and dashed lines, respectively

e.g. Breck 1974), the main source of excess protons at high temperatures is provided by H_2O molecules coordinating Ca^{2+} . The interaction of these protons with framework oxygen atoms may give rise to two different types of the stable protonic defects: terminate OH group, arising as a result of breakage of oxygen bridges T–O–T, and Brønsted centers, accompanied by the formation of CaO molecules or/and $[\text{Ca–O–Ca}]^{2+}$ complexes. As residual H_2O is removed from the zeolite cavities, the irreversible accumulation of such defects is gradually terminated, but restarts with new dehydration cycle. It is well to bear in mind that the retention of the rate of accumulation of the acid sites with cycles corresponds to the situation when the concentration of these defects remains very low, as in our experiments. However, one cannot expect the same linear growth of the HZ concentration when the latter becomes larger, though so far the limit of linearity is unknown.

Summary

Applying a new NMR approach, together with an IR-spectroscopy CO-probe method, we have investigated the response of a framework mineral clinoptilolite to thermal treatment. It was found that recurring dehydration of Ca-rich clinoptilolite leads to the accumulation of the active acid sites (chemical defects) on the internal surface of the crystal. The amount of these defects, accumulated during several dehydration-rehydration cycles, seems too small to be responsible for any changes in the crystal structure or in the absorption properties of zeolite; however, it is sufficient to induce a remarkable enhancement of the rate of the proton-transfer reaction in the cavities, and consequently, to modify the properties closely related to the active sites, such as catalytic activity and proton conductivity.

The activation energy of the reversible proton-transfer reaction between water molecules and the excess protons localized on the bridging oxygen atoms in the clinoptilolite structure is 46 kJ mol^{-1} , thus falling in the range of the corresponding activation energies ($45\text{--}60 \text{ kJ mol}^{-1}$) determined recently (Afanassyev et al. 2000) for the various ion-substituted forms of zeolite chabazite.

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References

- Afanassyev IS, Moroz NK, Belitsky IA (2000) Proton transfer in hydrated microporous aluminosilicates: a ^1H NMR study of zeolite chabazite. *J Phys Chem (B)* 104: 6804–6808
- Armbruster T (1993) Dehydration mechanism of clinoptilolite and heulandite: single-crystal X-ray study of Na-poor, Ca-, K-, Mg-rich clinoptilolite at 100 K. *Am Mineral* 78: 1872–1883
- Armbruster T, Gunter ME (1991) Stepwise dehydration of heulandite–clinoptilolite from Succor Creek, Oregon, USA: a single-crystal X-ray study at 100 K. *Am Mineral* 76: 1872–1883
- Bish DL (1995) Thermal behavior of natural zeolites. In: Ming DV, Mumpton FA (eds) *Natural zeolites '93*. Brockport, New York, pp 259–269
- Breck DW (1974) *Zeolite molecular sieves*. Wiley, New York, pp 410–523
- Ducros P (1960) Étude de la mobilité de l'eau et des cations dans quelques zéolites par relaxation diélectrique et résonance magnétique nucléaire. *Bull Soc Fr Mineral Cristallogr* LXXX-III: 85–112
- Carron O, Chevreau T, Havalley JS (1998) Brønsted acidity of extraframework debris in steamed Y zeolites from the FTIR study of CO adsorption. *J Chem Soc Farad Trans* 94: 3039–3042
- Colluccia S, Marchese L, Martra G (1999) Characterization of microporous and mesoporous materials by the adsorption of molecular probes: FTIR and UV-Vis studies. *Micropor Mesopor Mater* 30: 43–56
- Gabuda SP, Lundin AG (1968) Diffusion of water in hydrates and NMR spectra. *Sov Phys JEPT* 55: 1066–1069
- Koyama K, Takéuchi Y (1977) Clinoptilolite: the distribution of potassium atoms and its role thermal stability. *Z Kristallogr* 145: 216–239
- Moroz NK, Kholopov EV, Belitsky IA, Fursenko BA (2001) Pressure-enhanced molecular self-diffusion in microporous solids. *Micropor Mesopor Mater* 42: 113–119
- Razdobarova NL, Paukshtis EA (1991) Acid properties of ZSM-5 zeolites after hydrothermal treatment at 540°C . *React Kinet Catal Lett* 43: 515–520
- Sobolev VI, Dubkov KA, Paukshtis EA, Pirutko LV, Rodkin MA, Kharitonov AS, Panov OI (1996) On the role of Brønsted acidity in the oxidation of benzene to phenol by nitrous oxide. *Applied Catalysis (A)*. General 141: 182–192
- Van Reeuwijk LP (1974) The thermal dehydration of natural zeolites. *Meded, Landbouwhogeschool, Wageningen* 74: 1–88